Department of Health Services

Reply to *DTSC Review, August 29, 2000* of Draft *Sampling and Analysis Plan for Phase 2 Sampling of Radionuclides in Groundwater at Former MCAS El Toro, July 17, 2000*

August 29, 2000

DTSC Resource Planning Form # 502

The following comments and questions are in response to the request from Ms. Triss Chesney of the Department of Toxic Substances Control to review the Draft *Sampling of Radionuclides in Groundwater at Former MCAS El Toro, July 17, 2000.* This document was reviewed by Deirdre Dement and Kurt Jackson of DHS.

General Comments:

1. The document does not discuss whether or not samples will be collected for chemical analytes such as general minerals and metals. While this work may be separate, any conclusions regarding the source of uranium found in groundwater rely heavily on the groundwater conceptual model and verification of it through sampling and analysis.

LLNL Reply: The utility of chemical composition data (major, minor and trace elements) in attributing the source of uranium to El Toro groundwaters has been discussed in internal conversation between the water districts and LLNL. A decision was made to first determine whether or not the uranium was natural or anthropogenic. Contrary to the comment the "conclusions regarding the source of uranium found in groundwater rely heavily on the groundwater conceptual model", precise determination of uranium isotopic composition will allow the first-order distinction between natural and anthropogenic (see LLNL Reply to General Comment 2 below). The methods being used to collect groundwater for uranium isotopic analysis are adequate for trace metal analysis, and sufficient volumes are being collected that waters can be preserved and archived for future trace metals analysis at LLNL

2. The Site background section on Page 3 discusses problems with the previous study noting that the uncertainty in uranium isotope ratios made it impossible to reach an absolute conclusion regarding whether the uranium is naturally occurring. It should be noted in the document that one of the goals of this study is to reduce the uncertainty in uranium isotope ratios, but that isotopic uranium analysis alone cannot support an absolute conclusion about the source of the uranium. The analysis proposed in this study should result in a much lower uncertainty in uranium isotope ratios. However, it also cannot conclude absolutely whether or not there is a contribution from depleted or enriched uranium. The point is that there may be a mixture of natural, depleted and/or enriched uranium, which will result in groundwater sample results that fall within the uncertainty in isotope ratios consistent with natural uranium. Therefore, any conclusions regarding the absence of depleted or enriched uranium rely heavily on the historical site assessment and the groundwater conceptual model.

LLNL Reply: The statement that precise uranium isotopic analysis alone "cannot conclude absolutely whether or not there is a contribution from depleted or enriched uranium" is incorrect. Uranium in occurs in nature as a mixture of three isotopes: ^{238}U, ^{235}U, and ^{234}U. The ratio of ^{235}U to ^{238}U in natural materials (with one exception) has been found to be constant at 0.00725 to within analytical measurement uncertainty. Determinations of this ratio in natural earth materials by different groups and different techniques agree to within 0.05%. The one exception is the Oklo uraninite deposit in Gabon, West Africa, where considerably lower ^{235}U contents have been ascribed to a natural fission reaction occurring at a time when ^{235}U was about 3 percent abundant some 1.8 billion years ago. This is probably a unique event in Earth history.

The primary source of processed uranium to the military, industry and research is the nuclear fuel cycle, and this uranium has a $^{235}U/^{238}U$ ratio which is either higher ("enriched") or lower ("depleted") than the natural ratio. Both are produced in the isotopic separation process by which uranium is enriched for use as nuclear fuel. Processed uranium also contains the non-naturally occurring isotope ^{236}U. Uranium-236 is produced in enriched-uranium nuclear reactors, and was introduced to the depleted uranium supply when "spent" uranium from nuclear reactors was "re-enriched" by isotope separation in the early 1950's. The long residence time of uranium in the Oak Ridge isotope separators means that all uranium produced in the last 50 years, whether enriched or depleted, is imprinted with ^{236}U.

As a consequence of these isotope systematics, the discovery of $^{235}U/^{238}U$ ratios in El Toro groundwaters which are measurably different from the natural ratio would require an anthropogenic source. We stress that the alpha spectroscopy determinations, because of the large uncertainties in quantifying the ^{235}U peak, are *not* statistically distinguishable from the natural ratio. The reviewers are concerned that mixing of enriched and depleted uranium could mimic natural uranium This concern is not justified on two counts: 1) since both depleted and enriched uranium contain ^{236}U, a mixture will also contain ^{236}U which will be detectable and does not occur naturally; 2) the mixing would have to be exact and unvarying for all analyzed waters to have natural ratios. The reviewers are also concerned that mixing "of natural, depleted and/or enriched uranium will result in groundwater sample results that fall within the uncertainty in isotope ratios consistent with natural uranium." This addresses an important point. The finding of natural uranium isotopic composition (natural $^{235}U/^{238}U$, ^{236}U not detected) in El Toro groundwaters does not preclude a small component of anthropogenic uranium but places a strong upper limit on such a contribution. If for example, if a groundwater were found to have natural $^{235}U/^{238}U$ ratios to within 1.5% (3-sigma), the detection limit for depleted U ($^{235}U/^{238}U$ atom ratio = 0.00200) would be ~2% of the measured ^{235}U content, and the detection limit for mildly enriched U ($^{235}U/^{238}U$ atom ratio = 0.03000) would be ~2% of the measured ^{235}U content. For sample LD-0009, which has the highest measured ^{238}U and ^{235}U activities at El Toro, these detection limits correspond to the addition of less than 0.5 pCi/L of anthropogenic U.

This discussion does not discount the need for a historical or geologic site assessment. Such an assessment can rule out the introduction of uranium from mining operations or from a natural nuclear reactor. Uranium from mining operations would be anthropogenic but have a natural isotopic composition. Uranium from a natural nuclear reactor would be "natural" but have an anomalous isotopic composition. The lack of historical records for uranium mining and the

uniquness of natural nuclear reactors, coupled with the absence of uraninite deposits in the area and age and geology of the sediments at El Toro preclude serious considerations of these scenarios.

3. Have any of the stakeholders reviewed the LLNL quality assurance data and samples of laboratory reports for this type of analysis? The results or conclusions of this review should be summarized in the document.

LLNL Reply: No certified techniques exist for the determination of uranium isotopic composition by mass spectrometry. LLNL can provide sample laboratory reports, and data showing the ability to accurately determine uranium isotopic composition in NIST-certified standards. We also can supply data pertaining to blanks and reproducibility..

Specific Comments:

1. Page 4, Sampling Objectives: This paragraph states that uranium concentration and isotopic composition will be measured by isotope dilution mass spectroscopy. This method is not mentioned under the analytical techniques section on Page 3. Plan should include further explanation of isotope dilution mass spectroscopy or a reference citation.

LLNL Reply: The paragraph mentions mass "spectrometry" not "spectroscopy". ICPMS is an instrumental technique, and can be used in a number of ways to determine the concentration of an element in an analyte solution: external calibration, standard additions, isotope dilution. In isotope dilution, the concentration of an element or isotope is determined by measuring its isotopic composition after the addition of a known amount of spike containing either an isotopically enriched form of the element or a non-naturally occuring isotope of the element. For uranium, the addition of non-naturally occuring ^{233}U to sample solution, the measurement of the $^{238}U/^{233}U$ atom ratio in the spiked solution, and the calculation of the ^{238}U concentration from this ratio constitute isotope dilution. Isotope dilution is an absolute technique, and is far more precise than the other techniques mentioned. This is primarily because of the the precision and accuracy with which isotope ratios can be measured. I agree that isotope dilution should be mention in the analytical techniques section, and should be defined at some point in the text.

2. Page 6, Sampling Equipment and Procedures, *Field Preservation*: Will the material filtered out (filtrate) be analyzed? Also, the basis for the decision to filter the samples should be specified in the document.

LLNL Reply: The use of cartridge filters precludes the recovery of filtered material, and filtrate will not be analyzed. Filtration gives a more accurate determination of the concentration and isotopic composition of the dissolved U component which will be the most mobile component in

groundwater transport. In oxidized groundwaters, the dominant aqueous species of U is a uranyl carbonate complex which will exist in the dissolved state.

3. Page 8, Sample Handling and Analysis, *Sample preconcentration and spiking:* The preconcentration and scavenging with iron hydroxide needs to be explained more clearly. Does the U-233 added before the iron hydroxide precipitation also act as a yield tracer for this chemical separation by scavenging? The iron hydroxide precipitation probably scavenges elements other than uranium. Is there any further chemical separation required after the iron hydroxide precipitation? The document should clarify this and explain why interference from other elements with similar mass isotopes will not be a problem.

LLNL Reply: The added U-233 does act a yield tracer for the iron hydroxide chemistry and any subsequent chemistry. Iron hydroxide precipitation scavenges a number of other elements. For ICPMS, these elements do not form atomic or molecular (oxide, argide, etc) ions which isobarically interfere with the determination of U isotopic composition.

4. Page 8, Sample Handling and Analysis, *Sample preconcentration and spiking:* The first sentence of the last paragraph of Page 8 specifies a procedure for samples containing less than 20 ng/ml of uranium. A sentence in the previous paragraph appears to specify a procedure for samples containing between 5 and 10 ng/ml of uranium. These two paragraphs should be reviewed and revised as needed for clarity and consistency.

LLNL Reply: The paragraphs will be reviewed and revised as needed.

5. Page 9, Sample Handling and Analysis, *ICPMS Uranium Isotope Method:* Are the mass bias corrections specified in the standard equations used in mass spectroscopy? It would be helpful to specify a reference for the equations or explain the basis for their use.

LLNL Reply: The mass bias corrections are standard in mass *spectrometry*.

6. Page 9, Sample Handling and Analysis, *ICPMS Uranium Isotope Method:* Is the uncertainty in the mass bias included in the reported uncertainty in isotope ratios for sample results? The equations used to calculate reported results and associated uncertainty estimates should be shown or referenced in the document. It would be helpful to include an example of a laboratory report from previous LLNL work as an attachment to the document. If this is not possible, stakeholders should at least review a sample report.

LLNL Reply: The uncertainty in the mass bias correction is not included in the reported uncertainty in isotope ratios for individual samples. The uncertainty in the mass bias correction is generally much less than the uncertainty. During each batch of samples, the U-500, and U-005 and/or U-010 NIST-certified uranium isotope standards are run at regular intervals. The U-500 standard is used to determine mass bias, the other two standards are used to monitor the

accuracy, precision and reproduciblity of the technique. The accuracy and reproducibility in repeated U-005 and U-010 runs addresses any uncertainty in mass bias correction. Sample reports are available.

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TRANSMITTAL LETTER

DATE: September 8, 2000

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1	Lawrence Livermore National Labs response to DTSC comments on Radionuclide Sampling and Analysis Plan (July 17, 2000)
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I hope these responses to comments will satisfy the DTSC so that we can proceed with the sampling. We are awaiting a tentative sampling schedule from you so that we can schedule our field staff. Regards.

BY Adam Hutchinson